SULPHUR SOLUBILITY

IN $CaO-Al_2O_3$ AND $CaO-Al_2O_3-CaF_2$ SLAGS

Shiro BAN-YA*, Mitsutaka HINO** Tetsuro KAJI***
and Takeshi ITOH****

* Professor Emeritus, Tohoku University, now Akita National College of Technology, Iijima, Akita, Akita 011 Japan
** Faculty of Engineering, Tohoku University, Aoba-ku, Sendai, Miyagi 980-77 Japan
*** Formerly Guraduate Student, Tohoku University, now Takasago Works, Asahi Glass Corp. Ltd., Takasago, Hyogo 676 Japan
****Formerly Guraduate Student, Tohoku University, now Chiba Works, Kawasaki Steel Corp., Chuo-ku, Chiba 260 Japan

SUMMARY

The sulphide capacity and solubility of sulphur at the temperatures from 1823 to 1923K were determined by chemical equilibrium observation between $CO-CO_2-SO_2-Ar$ and the CaO based slags of $CaO-Al_2O_3$ and $CaO-Al_2O_3-CaF_2$ systems, which are major slag systems of the secondary refining process.

The solubility increased with increasing CaO and replacement of Al_2O_3 by CaF_2. From the result obtained, it was made clear that sulphide capacity deviated from a constant value with increase of sulphur content in slag. This means that sulphur in slag does not show the Henrian behavior at high content of sulphur and that sulphide capacity might not always be an real index of slag basicity.

1. INTRODUCTION

Various kinds of the ladle refining processes have been developed these two decades to make high purity steel and to reduce the slag amount formed during smelting. Many kinds of fluxes have been developed and proposed to apply in the refining process. However, it is considered that the most important fluxes in the refining are CaO-based fluxes in view of economics, natural resources and environmental problems.

The addition of CaF_2 and Al_2O_3 to CaO powerfully lowers the melting point of solid CaO, and these three kinds of CaO-based fluxes of $CaO-CaF_2$, $CaO-Al_2O_3$ and $CaO-Al_2O_3-CaF_2$ systems have high basicity. Therefore, they are the major slags for desulphurization in the ladle refining. In the present work, the sulphide capacity and sulphur solubility for these slags have been measured to deepen the complete understanding of these refining processes.

2. EXPERIMENTAL

Figure 1 shows the experimental apparatus for the measurement of sulphur solubility in slag. It consisted of the purification train of Ar, $Ar-SO_2$ and $CO-CO_2$ gas mixtures, an alumina tube (0.07x0.06x1.00m) as a reaction chamber, and the vertical type Keramax electric resistance furnace (10 kVA) for a heating device, and the quenching zone for samples. Two sets of pt.6%Rh-Pt.30%Rh thermocouples were used. One of them was inserted between heating elements and the reaction tube and was connected to a temperature controller, and the other was set just above the crucibles to monitor the experimental temperature. The premelted synthetic $CaO-Al_2O_3$ or $CaO-Al_2O_3-CaF_2$ slags of 1x10-3kg set in three Pt (0.01x0.01m) or two CaO 0.015x0.013x0.015m) crucibles loaded in a MgO protective crucible (0.035x0.030x0.01m) were melted under the given $CO_2-CO-SO_2-Ar$ mixed gas ratio of the flow rate of 2.5x10-6m3/s. The samples were held for 4-6h at 1823, 1873 or 1923K.

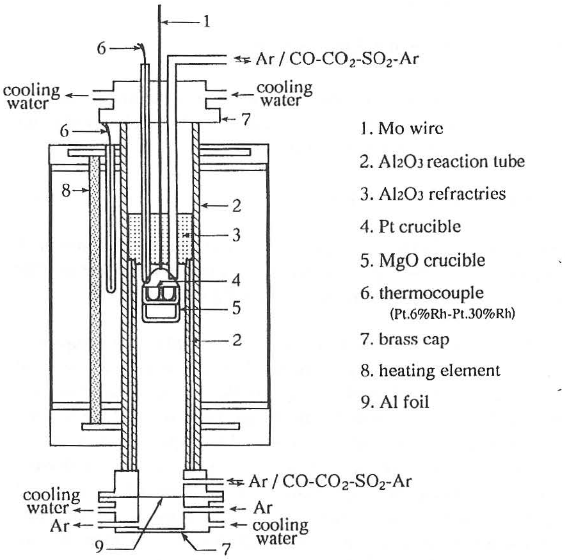

Fig. 1. Experimental apparatus for measurement of sulphur solubility.

At the end of run, the MgO crucible containing the samples in Pt or CaO crucibles was lowered with the Mo wire to a water-cooled chamber of Ar atmosphere to quench the samples. The slags were separated from quenched crucibles, and the contents of CaO, Al_2O_3, CaF_2 and S in the slags were determined by chemical analysis.

The Pt crucibles were hand-made from Pt foil , of which thickness was 5x10-5m, by forge welding, and the CaO and MgO crucibles were bought from a market. The gas mixtures were supplied by two kinds of cylinder of CO_2-50.1vol%CO and Ar-1.987vol%SO_2.

3. RESULTS AND DISCUSSION

3.1. Definition of Cs and Cs'

The principal equilibrium reaction between gas and slag is expressed by Eq. (1) after Richardson et al.[1)] on the condition of $P_{O_2} \leqq 10^{-6}$atm such as present work.

$$1/2S_2(g) + (O^{2-}) = (S^{2-}) + 1/2O_2(g) \qquad (1)$$

Richardson et al. assumed the Henrian behavior of sulphur in slag because of its low solubility, and defined the following sulphide capacity, C_S, to discuss the physico-chemical property of slag.

$$C_S = (\text{mass\%S})(P_{O_2}/P_{S_2})^{1/2} \quad (2)$$

$$= K_1 a_{O^{2-}}/f_{S^{2-}} \quad (2)'$$

Where, (mass%S) means the mass% of sulphur concentration in slag.

Equation (1) is represented with Eq. (3) by use of molecular theory instead of ionic theory.

$$1/2S_2(g) + (CaO) = (CaS) + 1/2O_2(g) \quad (3)$$

If pure substances were adopted as the standard states of activities of CaO and CaS, molar sulphide capacity, C_S', is defined.

$$C_S' = N_{CaS}(P_{O_2}/P_{S_2})^{1/2} \quad (4)$$

$$= K_3 a_{CaO}/\gamma_{CaS} \quad (4)'$$

3.2. Determination of Sulphur Solubility

There are two methods for determination of sulphur solubility. One is the following method. Equation (5) is obtained from logarithm of both hand sides of Eq. (4).

$$\log C_S' = \log N_{CaS} + 1/2\log(P_{O_2}/P_{S_2}) \quad (5)$$

As the slope of $\log C_S'$ vs $\log N_{CaS}$ shows 1/2 beyond saturation of sulphur for a given slag composition, we can determine the sulphur solubility from the bending point in the figure.

Another method is as follows. For example, five samples in CaO-(1-x)Al_2O_3-$x$$CaF_2$ systems, as shown in **Fig. 2**, are reacted with a given gas potential P_{O_2}/P_{S_2}. If No.1 to No.3 samples were assumed to be equilibrated with the gas potential and the sulphur content did not extend the solubility, the iso-gas potential line is drawn with a smooth curve as shown Fig. 2. If No.4 and No.5 samples saturated with sulphur under the gas potential, the chemical analysis results of slag compositions exist on the D', D" or E', E" points, which depends on the experimental time. Therefore, we can determine the sulphur solubility, such as a bold dashed line in Fig. 2, from the cross points of smooth gas potential lines and lines tied sulphur saturated slag composition and CaS.

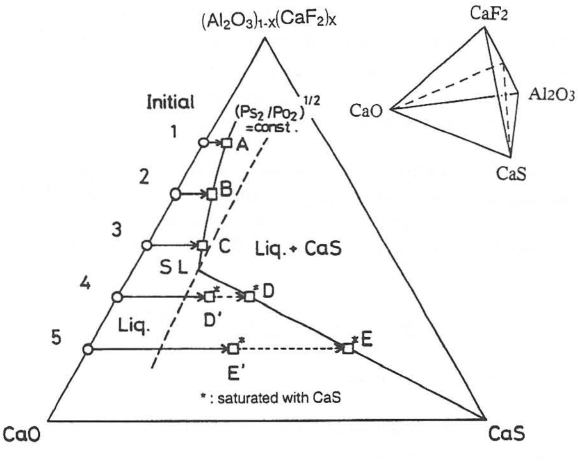

Fig. 2. Method of determination of sulphur solubility.

3.3. Sulphur Solubility in Slag

In the present work, the latter method is adopted, because $\log C_S'$ is not constant against $\log N_{CaS}$, especially near the sulphur saturation, as mentioned later.

3.3.1. CaO-Al_2O_3 System

Figure 3 shows the result of iso-gas potential curves and sulphur solubility limit, which is reperent by reagion with arrow because of experimental uncertainty, in CaO-Al_2O_3 system obtained at 1873K in the present work.

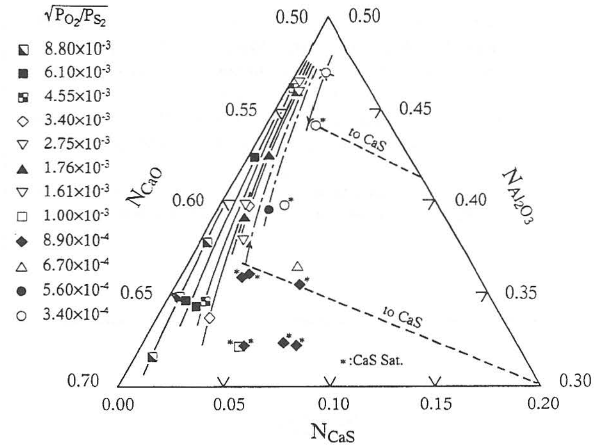

Fig. 3. Iso-gas potential lines of $(P_{O_2}/P_{S_2})^{1/2}$ in CaO-Al_2O_3 slag at 1873K.

The solubility has been determined in this system at 1823, 1873 and 1923K in the present work. But, the temperature dependence of liquidus of primary CaS in CaO-Al_2O_3-CaS system has not been distinguished because of the experimental uncertainty as shown in **Fig. 4**, where the other investigator's results are compared. Present result is consistent with those after Richardson et al.[2),3)].

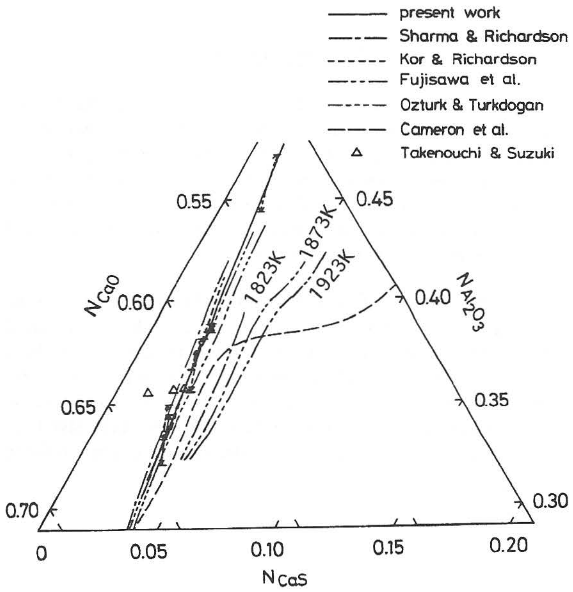

Fig. 4. Sulphur solubility in CaO-Al_2O_3 slag.

3.3.2. $CaO-Al_2O_3-CaF_2$ System

In this paper, the sulphur solubility is observed on the planes of $CaO-(1-x)Al_2O_3-xCaF_2$ system, where $x = 0.16$, 0.23, 0.37 and 0.46. **Fig. 5** shows an example of results of iso-gas potential curves and sulphur solubility obtained at 1873K in $CaO-0.54Al_2O_3-0.46CaF_2$ system in the present work. The diagram is projected on the plane of $CaO-Al_2O_3-CaS$ system.

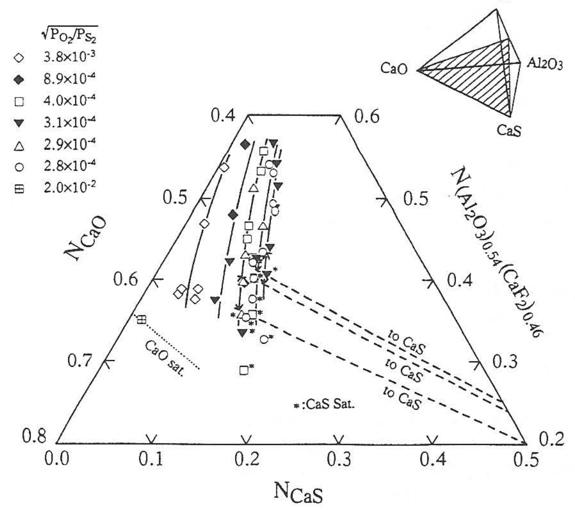

Fig. 5. Iso-gas potential lines of $(P_{O_2}/P_{S_2})^{1/2}$ in $CaO-0.54Al_2O_3-0.46CaF_2$ slag at 1873K.

Hawkins et al.[4] measured the sulphur solubility in $CaO-CaF_2$ system at 1773 and 1823K. But their liquidus of primary CaS at 1823K extended to $CaO-CaF_2$ binary side compared with that at 1773K. Therefore, the discrepancy Is modified by present authors. As the results, the sulphur solubility at 1873K in $CaO-(1-x)Al_2O_3-xCaF_2$ system has been evaluated based on the present observation and the above-mentioned estimation in $CaO-CaF_2$ system. The result is shown in **Fig. 6**. The solubility of CaS in $CaO-Al_2O_3$ slag is only 1.5-4mol%, and it increases with CaO content. However, the solubility increase markedly with replace of Al_2O_3 to CaF_2, it reaches to 27mol%CaS in $CaO-CaF_2$ slag, as shown in Fig. 6.

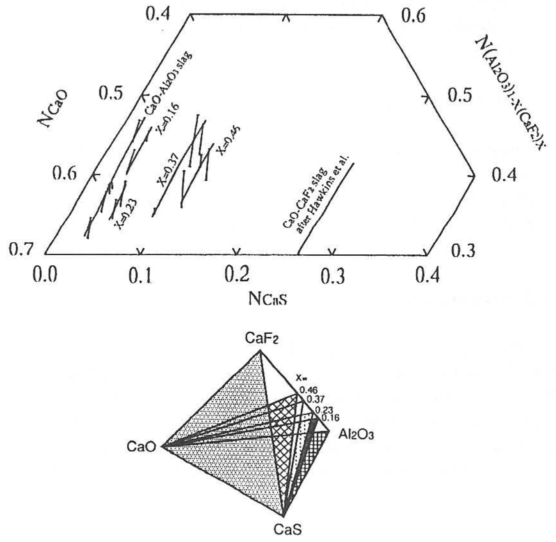

Fig. 6. Effect of CaF_2 addition on the sulphur solubility in $CaO-Al_2O_3$ slag at 1873K.

3.4. Molar Sulphide Capacity

If dissolved sulphur in slag shows Henrian behaviour as mentioned generally, $\log C_S$ for a given slag composition will be a constant against $\log N_{CaS}$ until sulphur solubility limmit in consideration of Eq. (5).

3.4.1. $CaO-Al_2O_3$ System

Figure 7 shows molar sulphide capacities of homogeneous, CaO-saturated and CaS-coexisted $CaO-Al_2O_3$ melts obtained at 1873K in the present work. The numerical value of *Cs*' in this slag increasesd with increasing concentration of CaO. The higher the temperature is, the more the value of *Cs*' increases.

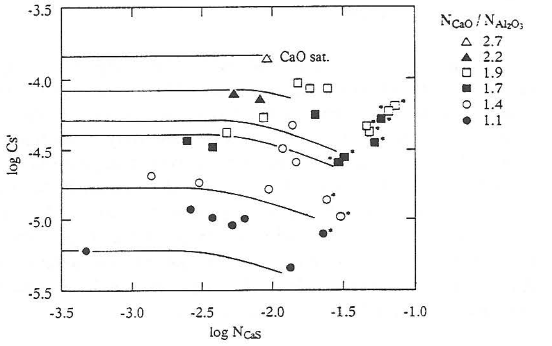

Fig. 7. Molar sulphide capacities in $CaO-Al_2O_3$ slag at 1873K.

The value of $\log C_S$ for a given slag composition in $CaO-Al_2O_3$ slag shows slightly negative deviation near sulphur saturated composition, but it is almost independent of $\log N_{CaS}$ until sulphur solubility limit, as shown Fig. 7. This means that dissolved sulphur almost shows Henrian behavior until sulphur saturation in this slag system.

The C_S in $CaO-Al_2O_3$ slag has studied at 1923K by Fincham and Richardson,[1] at 1923 and 1873K by Ozturk and Turkdogan,[5] at 1873K by Schurmann et al[6] on the condition of CaO or $CaO·2Al_2O_3$ saturation, at 1823K by Cameron et al.,[7] and at 1773K by Carter and Macfarlane[8], Sharma and Richardson,[2] and Kor and Richardson.[3] They agree well with the C_S obtained in the present work.

3.4.2. $CaO-Al_2O_3-CaF_2$ System

The molar sulphide capacities of homogeneous, CaO-saturated and CaS saturated $CaO-Al_2O_3-CaF_2$ melts were determined at 1873 on the condition of the given ratios of $N_{CaO}/N_{Al_2O_3}$, molar ratio of CaO to Al_2O_3, as 1.4 to 3.9, on the planes of $CaO-(1-x)Al_2O_3-xCaF_2$ system, where $x = 0.16$, 0.23, 0.37 and 0.46. **Fig. 8** shows an example of C_S' obtained at 1873K in $CaO-0.54Al_2O_3-0.46CaF_2$ system in the present work. It was found from Fig. 8 that the value of *Cs*' increased with increasing $N_{CaO}/N_{Al_2O_3}$, at a given temperature.

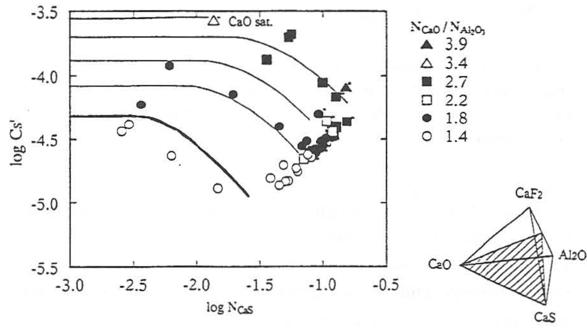

Fig. 8. Molar sulphide capacities in CaO-0.54Al_2O_3-0.46CaF_2 slag at 1873K.

The sulphur solubility in CaO-Al_2O_3-CaF_2 slag shows high value as mentioned in Fig. 6. The value of $\log C_S'$ for a given slag composition in this system shows obvious dependence on $\log N_{CaS}$ as shown Fig. 8, and the C_S' shows a constant only in the limited infinite dilution of sulphur. Therefore, dissolved sulphur does not show Henrian behavior in case of high sulphur content in slag. This means that sulphide capacity, generally speaking, depends on sulphur content in slag and is not proportionate to activity of free oxygen ion or activity of CaS in slag in consideration of Eqs.(2)' and (4)'. It concludes deductively that sulphide capacity does not act as a real index of slag basicity.

Based on the obtained results in very low sulphur concentration region where C_S' is considered to be a constant in the present work, molar sulphide capacities in CaO-Al_2O_3-CaF_2 slag are evaluated at 1873 K, which are shown in **Fig. 9**. Cs' in this slag increases with increasing CaO content at a constant $N_{Al_2O_3}/N_{CaF_2}$ and with replacing Al_2O_3 by CaF_2. The C_S of this slag was reported by Kor and Richardson[3)] at 1773K.

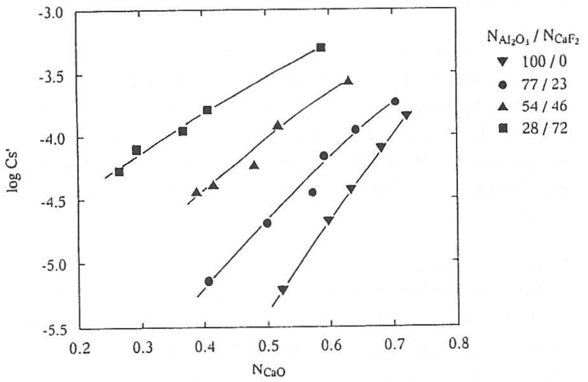

Fig. 9. Molar sulphide capacities in CaO-Al_2O_3-CaF_2 slag at 1873K.

3.5. Activity Coefficient of CaS in CaO-Al_2O_3-CaF_2 Slag

Activity of CaS is a unity when slag is saturated with sulphur. Therefore, the activity coefficient of CaS can be estimated with Eq. (6) by means of the slag composition saturated with sulphur.

$$\gamma_{CaS} = 1/N_{CaS_{sat.}} \qquad (6)$$

Where, $N_{CaS_{sat.}}$ is molar fraction of CaS in slag saturated with sulphur. The values of γ_{CaS} are estimated in the CaO-Al_2O_3-CaF_2 slag based on the sulphur solubility limmit observed in the present work shown in Fig. 6, and their iso-activity coefficient curves are shown in **Fig. 10**.

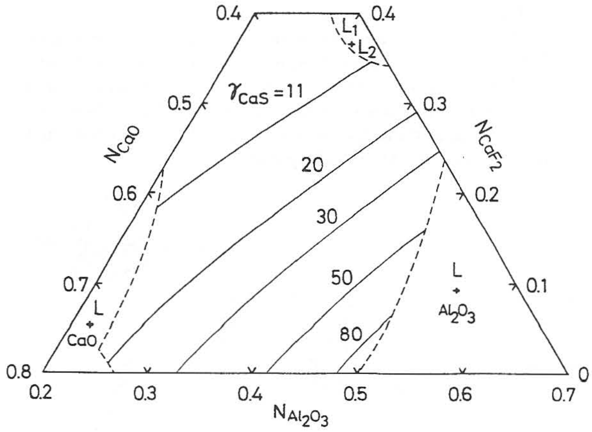

Fig. 10. Iso-activity coefficient lines of CaS in CaO-Al_2O_3-CaF_2 slag saturated with CaS at 1873K.

It is very clear from Fig. 10 that γ_{CaS} is a function of slag composition. This means again that sulphide capacity is not in proportion to activity of free oxygen ion or activity of CaS in slag in consideration of Eqs.(2)' and (4)' and it does not act as a real index of slag basicity, even if independent sulphide capacity of sulphur content is adopted.

4. CONCLUSIONS

The chemical equilibrium between CO-CO_2-SO_2-Ar gas mixtures and CaO-Al_2O_3, CaO-Al_2O_3-CaF_2 slags has been studied to determine the sulphide capacities and sulphur solbility of these slags, and the followings have been confirmed from the results obtained.

1) The sulphide capacities of these slags increased with increasing temperature and the concentration of CaO, and these increased with replacing Al_2O_3 by CaF_2.

2) Molar sulphide capacity for a given slag composition is almost independent of sulphur content in dilute solution. This means that dissolved sulphur shows Henrian behaviour in dilute sulphur content reagion.

3) Activity coefficient of CaS is a function of slag composition.

4) Sulphide capacity is the functional value of slag composition and sulphur concentration in slag. Therefore, it is not in proportion to activity of free oxygen ion or activity of CaS in slag, and it is not a real index of slag basicity.

Acknowledgements

The authors wish to thank Messrs. M. Hobo, Daidou Steel Co., Ltd., Y. Suzuki, Nippon Metal Industry Co., Ltd., and T. Kanemura, Ryobi Co., Ltd., for their effective assistance in making their experiment. A part of the experimental work was supported by the Grant-in-Aid for Scientific Research (C) from The Japanese Ministry of Education, Science and Culture, in 1993 and 1994.

REFERENCES

1. C.J.B.Fincham and F.D.Richardson : "The behaviour of sulphur in silicate and aluminate melts", Process Royal Society A, Vol.223, 1954, pp.40-62.; "Sulphur in Silicate and Aluminate Slags", Journal of the Iron Steel Institute, Vol.178, September 1954, pp.4-14.

2. R. A. Sharma and F. D. Richardson : "Activities in lime-aluminate melts", Journal of the Iron Steel Institute, Vol.198, 1961, pp. 386-390.

3. G. J. W. Kor and F. D. Richardson : "Sulfide Capacities of Basic Slags Containing Calcium Fluoride", TRANSACTIONS OF THE METALLURGICAL SOCIETY OF AIME, Vol.245, February 1969, pp. 319-327.

4. R.J.Hawkins, S.G.Meherali and M.W.Davies : "ACTIVITIES, SULPHIDE CAPACITIES, AND PHASE EQUILIBRIA IN CaF$_2$-BASED SLAGS", Journal of the Iron Steel Institute, Vol.209, August 1971, pp.646-657.

5. B. Ozturk and E. T. Turkdogan : "Equilibrium sulfur distribution between molten calcium aluminate and steel, Part 1", Metal Science, Vol.18, 1984, pp. 299-306, B. Ozturk and E. T. Turkdogan : "Equilibrium sulfur distribution between molten calcium aluminate and steel, Part 2", Metal Science, Vol.18, 1984, pp. 306-309, .

6. E. Schurmann, R. Bruder, K. Nurnberg and H. Richter : "Beitrag zur Schwefelloslichkeit in CaO-Al$_2$O$_3$-Schlacken", Archiv fur das Eisenhuttenwesen, Vol.50, 1979, pp. 139-143.

7. J. Cameron, T. B. Gibbons and J. Taylor : "Calcium sulphide solubilities and lime activities in the lime-alumina-silica system", Journal of the Iron Steel Institute, Vol.204, 1966, pp. 1223-1228.

8. P. T. Carter and T. G. Macfarlane : "Thermodynamics of Slag System", Journal of the Iron Steel Institute, Vol.185, January 1957, pp. 54-65.